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Spectra of Lead Hydride and Tin Hydride in the Near Infra-Red

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Revised calculations of energy constants of the PbH molecule are presented as a result of analyses of bands in the photographic infra-red. Former v' values are raised by one unit. An isolated weak PbH band is found at 3815A. Additional SnH bands in the red produced in the high pressure arc are briefly discussed.

In previous reports[1, 2] on the spectra of PbH and SnH in the visible, the probable existence of spectra of both these molecules in the photographic infra-red was mentioned. With further development of the high pressure arc in hydrogen, together with long exposure times and wider slit widths, PbH bands have been recorded to 9105A and SnH bands to 7234A. In addition, careful search for the PbH analog of the violet $^2\Delta\rightarrow{}^2\Pi$ SnH bands reveals a single weak band centered at 3815A. This band is not well developed and is not accompanied by another at any plausible interval for a $^2\Pi$ PbH state.

The Pb and Sn arcs have been run in hydrogen at 4 to 5 atmospheres pressure. All spectrograms were obtained in the second order of a 21-foot grating, average dispersion 2.13A per mm, except those of PbH for wave-lengths longer than 7200A. For the latter the first order with 4.94A per mm was used. Because of the wide-open structure of these hydride spectra, however, this lower dispersion was quite sufficient despite the considerable line widths due to pressure broadening and to the use of a wide slit (0.1 mm).

It was thought that bands involving a new electronic state of PbH might be located in the infra-red, since strong interaction with other states is revealed[1] by the details of the red $^2\Sigma\rightarrow{}^2\Sigma$ system. We find, however, that the extensive PbH spectrum in the infra-red to 9100A belongs completely to this same system. With the inclusion of the data from the analysis of these new bands, plus additional lines in previ-

Table I. *Additional bands in the* $^2\Sigma\rightarrow{}^2\Sigma$ *system of* PbH. *cm*$^{-1}$ *units; d denotes fused lines.*

	(0,2)				(0,3)				(0,4)				(1,3)			
K''	P_1	R_1	P_2	R_2	P_1	R_1	P_2	R_2	P_1	R_1	P_2	R_2	P_1	R_1	P_2	R_2
3		14,543.3							11,800.3		11,808.9					
4		529.3*d*	14,504.0						778.1	11,823.4	790.4	11,831.6				
5		511.6	476.1		13,072.8	13,128.7	13,090.6		751.9	808.9	768.2	819.4	13,555.7		13,575.7	
6	14,422.2*d*	489.0	446.6	14,506.9*d*	042.9	109.6	063.2	13,124.6	723.4	790.4	742.7	803.3	527.4		551.4	
7		462.7	411.1	482.0	008.9	086.1	031.9	102.3	691.7	768.2	712.9	783.4			522.3	
8	344.9*d*	431.5*d*	373.3	453.9	12,970.9	056.9	12,997.2	076.5	656.4	742.7	679.7	759.8	460.2		489.4	
9	301.0*d*	396.7	331.9	420.5	929.2	024.5	957.4	046.3	617.5	712.9	643.1	732.5*d*	420.4*d*	13,520.4	452.7	13,547.8
10	251.7	357.0	285.1	383.6	883.4	12,988.0	913.8	012.3	574.8	679.7	602.7	701.1	376.5	486.9	412.2	517.1
11	199.5	312.6*d*	234.8	342.2	833.5	947.3	866.4	12,973.9	528.4	642.3	558.4	666.3	329.5	449.1	367.8	481.9
12		264.5	180.3	296.2	779.6	902.4	814.9	931.3	478.5	601.2	510.5	626.7	278.3	407.4	319.6	442.7
13	080.9	212.0	121.1	245.5	721.9	853.5	759.6	884.4	424.6	556.2	458.7	583.7	223.5	361.6	267.5	399.4
14	013.5	154.5	057.4	191.5	660.1	800.3	699.7	833.5	367.2	507.6	403.0	537.0	164.9	311.7	211.2	351.7
15	13,943.8	*090.8*d*	13,989.4	131.6	594.3	743.2	636.1	778.3	306.0	454.9	343.6*d*	486.0	102.4*d*	257.4	150.8	300.1
16	869.9*d*	026.5	917.2	066.8	524.4	681.7	568.3	719.0	241.2	398.6	280.6	431.3	035.7	199.2	086.1	243.6
17	790.4	13,956.2*d*	840.3	13,999.5	450.6	616.1	496.4	655.1	172.9*d*	338.2	213.9	372.6	12,964.8	136.8	018.0	183.3
18	707.0	880.5	759.2	926.2*d*	372.5	546.3	420.1*d*	587.2	100.6	274.1	143.3	309.9	890.0	068.4	12,945.2	118.0
19	619.6	800.9	673.6	848.4	290.7	472.4	340.3	515.0	024.5	206.1	069.0	243.5	811.4	12,997.2	868.3	049.8
20	527.4*d*	716.8	583.7	766.3	204.9	394.2	256.2	438.7*d*		134.3	10,990.3	172.9*d*	726.8*d*	921.8	787.2	12,973.9*d*
21	431.2*d*	628.2	489.4	679.8	114.8	312.0		358.1		058.6		098.9	640.3	841.7	702.5	896.2
22		535.1	391.0	588.5	021.1	225.6	075.8	273.4		10,979.4		020.9	548.8	757.3	611.2	813.7
23		438.2	288.6		11,923.4	135.4	11,979.7	184.6					453.2	668.2	517.9	726.8*d*
24		336.3	181.1		821.8	041.1*d*	879.6	091.7					353.4	574.7	420.1*d*	635.0*d*
25		230.3			716.4	11,942.4	775.7	11,994.8					249.4	476.9	317.6	539.0
26						840.0*d*	667.8	894.4					141.1	374.7	211.0	438.7*d*
27						733.4*d*							028.4	268.0	100.6*d*	333.7
28													11,911.9		11,985.4	224.6
29													791.2	041.1*d*	866.3	110.8*d*
30													666.3*d*	11,921.9		11,992.9
31													537.1*d*			871.2
32													404.5			745.2

* Perturbed.

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[1] W. W. Watson, Phys. Rev. **54**, 1068 (1938).

[2] W. W. Watson and R. Simon, Phys. Rev. **55**, 358 (1939).

TABLE II. *Corrected* PbH *band origins.* $^2\Sigma \rightarrow {}^2\Sigma$.

v'	$v''=0$		1		2		3		4
0					14,551.1	1388.5	13,162.6	1324.9	11,837.7
					479.0		478.6		
1	17,977.4	1503.1	16,474.3	1444.2	15,030.1	1388.9	13,641.2		
	448.2		448.1		448.0				
2	18,425.6	1503.2	16,922.4	1444.3	15,478.1				
	438.9		438.1						
3	18,864.5	1504.0	17,360.5						
	432.6								
4	19,297.1								
5	(19,700)								

ously analyzed bands, revision of the calculation of the energy constants[1] for PbH is necessary.

RED AND INFRA-RED PbH SPECTRUM

Assignments of the lines of four additional bands at the red end of this system are included in Table I. This analysis is based on the usual combination relations and indicates that the v' numbering of all the bands described in reference 1 should be increased one unit. The results of a recomputation of all band origins are given in Table II. Since we can find no traces of bands that would extend this array upwards, we believe that these vibrational quantum numbers are now correct. New constants of the energy terms are collected in Table III.

TABLE III. *Constants of the energy terms for* PbH *in* cm^{-1} *units.*

CONSTANT	$^2\Sigma'$	$^2\Sigma''$
B_0^*	2.478	4.899
B_1^*	2.660	4.754
B_2^*	2.766	4.609
B_3^*	2.770	4.467
B_4^*	2.646	4.324
B_e^*		4.971
α		0.144
r_0		1.848A
D_0	-2.66×10^{-4}	-2.01×10^{-4}
ω_e	$\sim$520	1564.1
$\chi_e\omega_e$		29.75
ν_e	$\sim$18018	

These data emphasize the peculiar nature of the upper $^2\Sigma$ state as discussed in reference 1.[3] The new B_0' being markedly lower than the old one, the tendency for the B_v' values to increase with v to a maximum and then to decrease is even more apparent. Since about 500 cm^{-1} are now added to the extent of the stable levels of this state, the cut-off of levels comes actually at about 0.42 volt above the bottom of the potential energy curve. These and the other peculiarities of this $^2\Sigma$ state all point to the existence of additional near-lying electronic states of PbH. The faint band at 3815A is, however, the only indication we can find of other PbH spectra. Because of competition from the continuous background always present in high pressure sources and which is particularly strong to the violet of the 4019 PbI atomic line, long exposure times do not yield better registrations of this band. For this reason and also because of its isolated character we have not attempted its analysis. We conclude that the only stable states of the PbH molecule are those involved in this red band system.

RED SnH SPECTRUM

SnH bands have been photographed further into the red than those already reported.[2] Prominent heads of the red-degrading branches occur at 6745, 6892 and 7030A with a pile-up of lines at 6931A. Between the latter and a long series of lines on its violet side, as well as between two other branches, we find $^2\Pi$-state combination differences.[2] We have not found differences relating these bands to the bands at 6095 and 6214A, however, and since the analysis of all these bands is far from complete we refrain from presenting it. They are definitely of a different type than those of the PbH system, probably $^2\Sigma \rightarrow {}^2\Pi$, judging from the number of branches. It is altogether probable that more SnH bands exist further into the infra-red. Their measurement should prove helpful in the analysis of the bands already photographed, but we find it impossible to obtain high dispersion spectrograms in the infra-red with the present high pressure Sn arc as a source.

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[3] Also cf. L. Gerö, Physica 7, 155 (1940).